CHAPTER 3

METHODOLOGY

3.1 Introduction

This research will be developed a technique to fabricate Bi_2Te_3- and PbTe-based samples using a hot press and its Seebeck coefficient properties will be measured under small and large temperature differences. Two approaches to preparing a mass of powder for fabricating the samples are being discussed. An improvised design of a homemade vacuum chamber is restructured to withstand high temperatures to allow measurement of Seebeck coefficient (α) properties under large temperature differences ($1\Delta T$).

3.2 Flow Chart

The study has been categorized into 3 main processes as shown in Figure 3.1 which are:

1) Fabrication of the thermoelement samples
2) Construction of the high-temperature measurement device
3) Measurement of Seebeck Coefficient

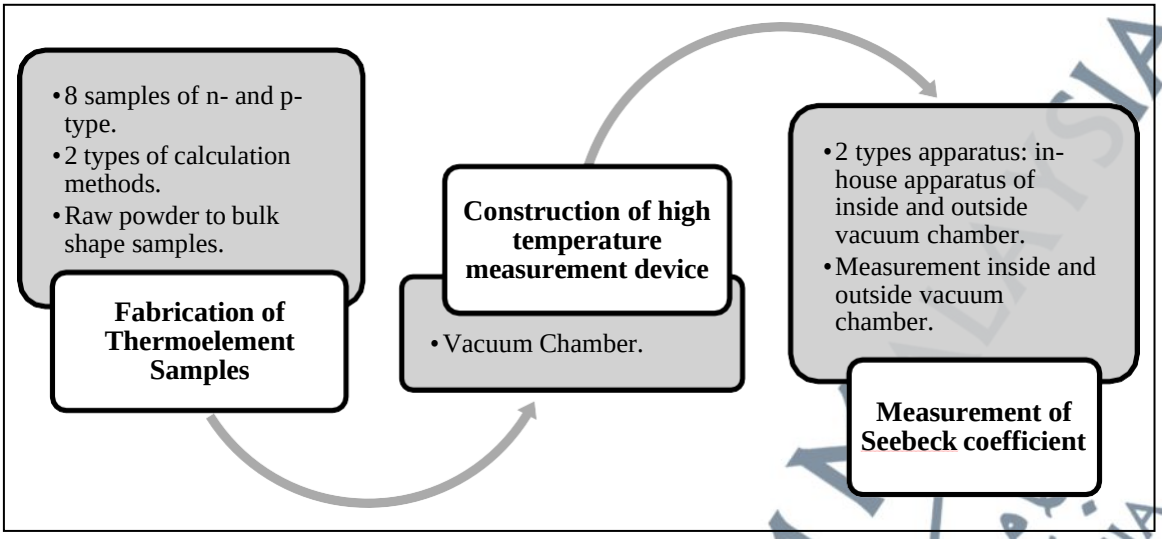

Figure 3.1: Flow Chart of research methodology

Figure 3.2 shows the details flow chart of this research methodology. A prototype of a high-temperature vacuum chamber will be developed based on a new improvised design to allow measurement α at lΔT. The improvement of the original design was made in 2012 which has limitation was the heat flow meter used become bent above the temperature of 540 K (Nadhrah MY, 2012). Therefore, the improvement in terms of replacing the heat flow meter with materials that can withstand high temperatures is made.

At the same time samples were prepared by calculating the weight of powder needed for desired compound ratio using 2 different methods. The first method is the atomic mass (AM) method which is based on stoichiometry in the calculation of the mass of the materials. The second method is using the volume ratio method (VR) based on density. The details of each method will be discussed in the next subtopic. Finally, the measurement of α under lΔT and sΔT will be made and compared. After that, the samples were fabricated using a hot press under different temperatures, pressure and pressing times.

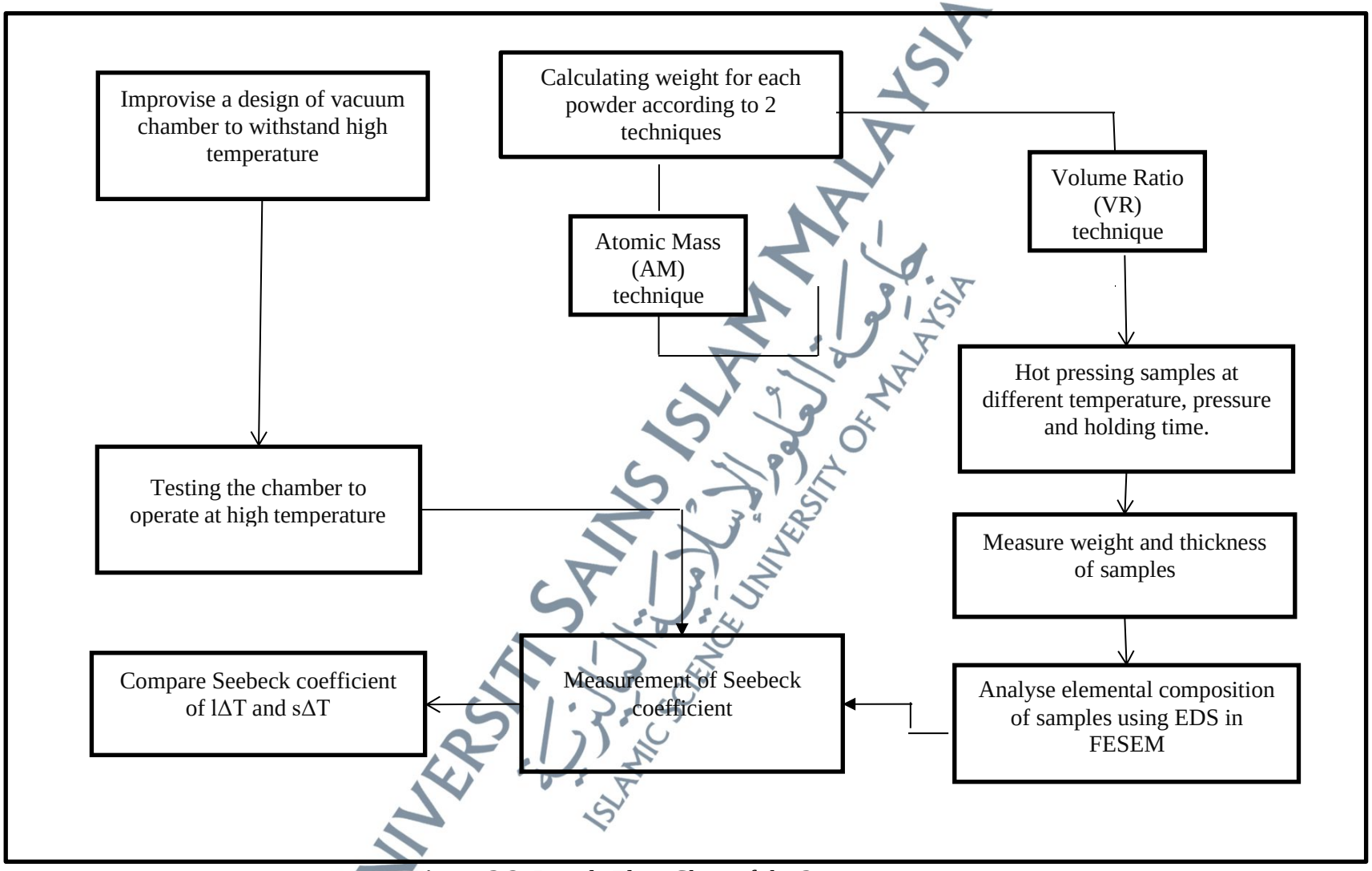

Figure 3.2: Details Flow Chart of the 3 main processes

3.3 Construction of High-Temperature Vacuum Chamber Apparatus

In 2012, an apparatus to measure the performance of single and segmented thermoelectric material has been developed. This apparatus was proved to have the ability to measure ZT using the open-short circuit method for samples at small and large temperature differences. It can also use to measure the thermoelectric properties of samples at high temperatures. However, at temperatures above 540 K the heat flow meter (brass) tends to be bent (Nadhrah M. Y., 2012). Thus, in this study, the improvement of the previous design is done so that it can operate at high temperatures.

The main concern of the new design is to make this apparatus can withstand high temperatures to measure Seebeck Coefficient. Therefore, instead of using the brass rod as a heat flow meter, tungsten was chosen as a replacement. Tungsten has the highest melting point of all metallic elements. Despite that, it is also known as the hardest metal below diamond. The highest melting point and hardest metal properties are characteristics that made tungsten the suitable material to use for this improvised apparatus. Table 3.1 shows several other apparatuses that will be used in the improvise apparatus. Although its thermal conductivity is 1.75 W/cmK which is lower than copper (4 W/cmK), however, tungsten is well known in the industry to have high electrical conductivity (about 28%) and the highest melting point of all metals (3695K). Figure 3.3 shows an outside view of the vacuum chamber as well as the pressure meter and thermocouple wires outside the vacuum chamber (Figure 3.4). Meanwhile, Figures 3.5 and 3.6 show the design and set-up of the apparatus in the chamber with thermocouples attached to the apparatus inside the vacuum chamber. Moreover, the real situation of apparatus setup with sample can be seen in Figure 3.7.

Table 3.1: Improvise Apparatus Design

APPARATUS	QUANTITY
Vacuum chamber	1
Vacuum pump	1
Thermocouples	6
Data logger	1
Multimeter	1
Cartridge Heater	1
Copper block	1
Tungsten heat flow meter	1
Flow water heat sink	1
Power supply	1

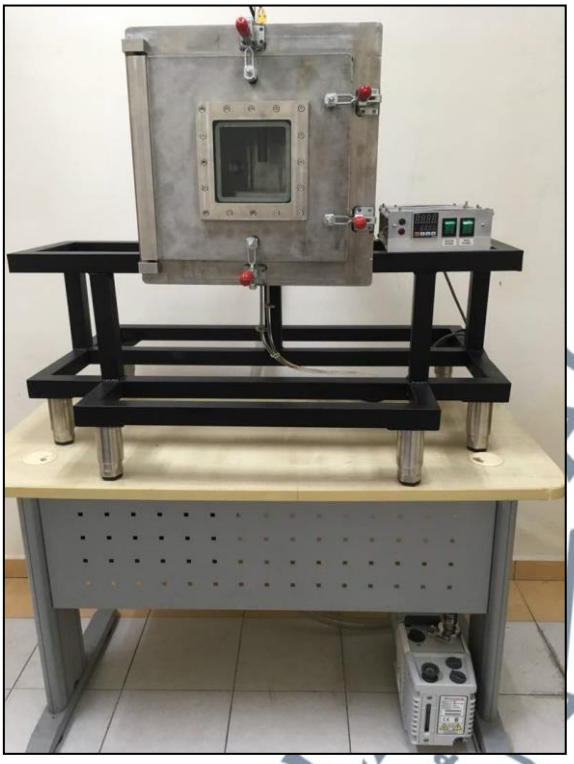

Figure 3.3: Outside view of the vacuum chamber

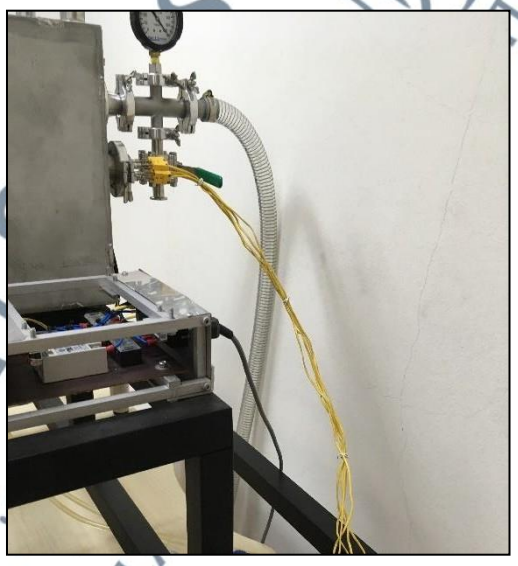

Figure 3.4: The pressure meter and thermocouples wire outside the vacuum chamber

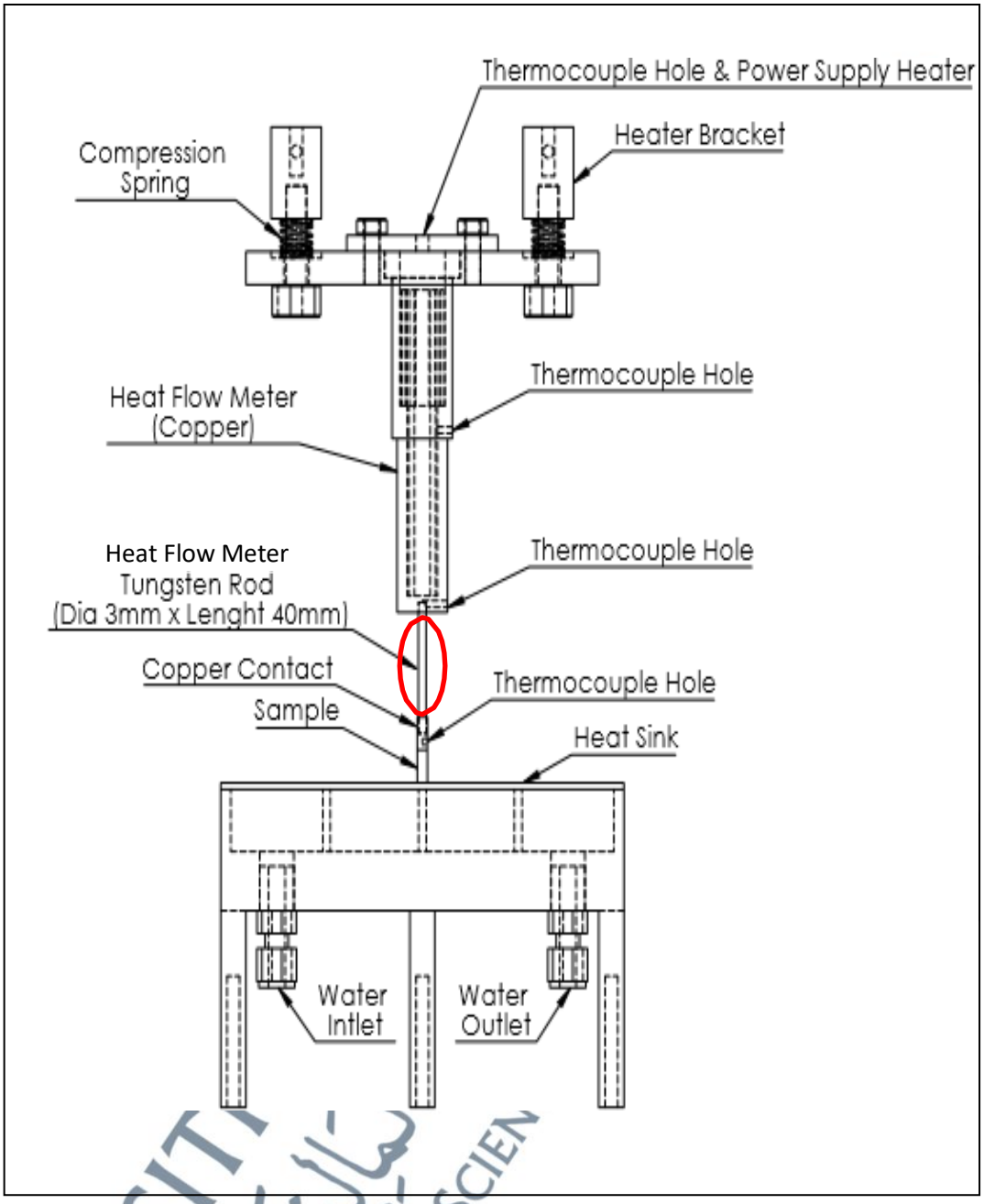

Figure 3.5: Apparatus setup

Figure 3.6: Apparatus setup with thermocouples attached

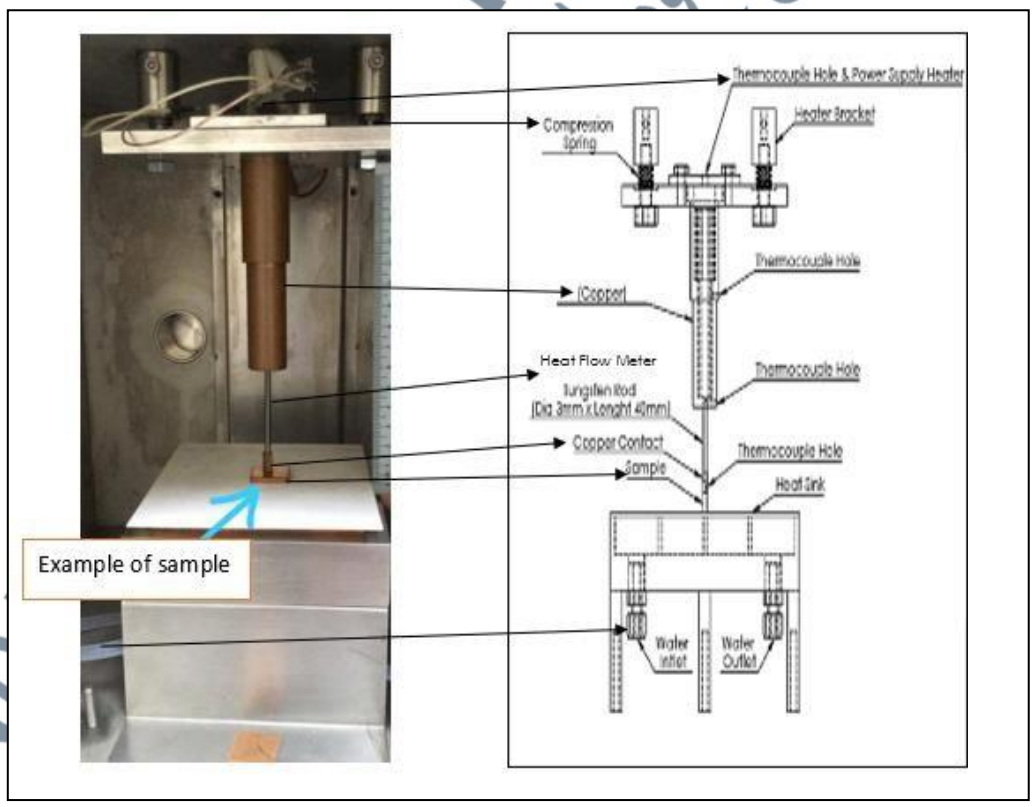

Figure 3.7: Real picture compared to the sketch design

The measurement of voltage for Seebeck is using a multimeter where the arrangement of wire is shown in Figure 3.8. The copper wire is connected to the multimeter through a feedthrough located at the back of the chamber. Water flow is used as the cold side of the arrangement. Before the process of measurement begin, the standard operating procedure (SOP) of the chamber needs to be followed.

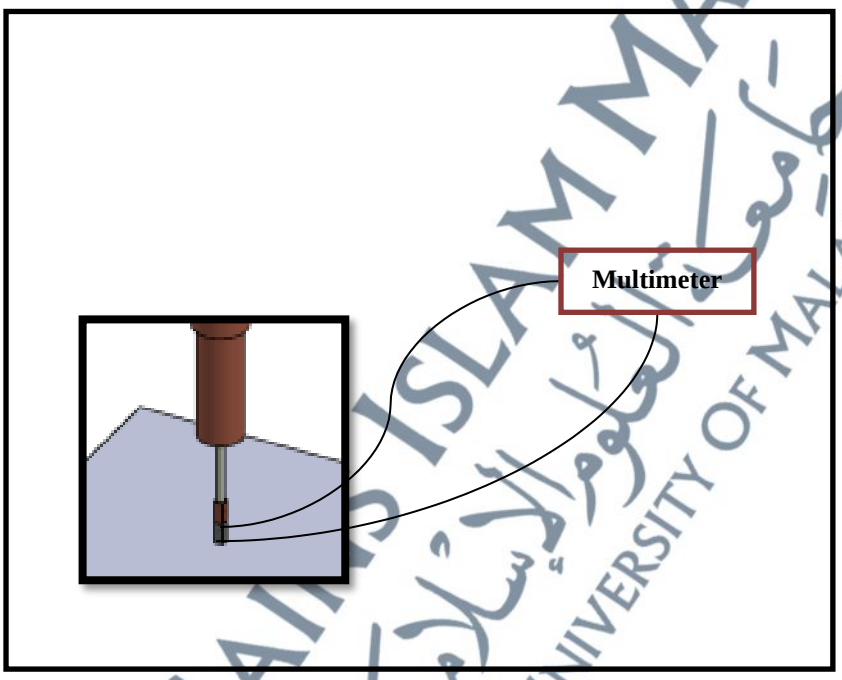

Figure 3.8: Arrangement of sample for Seebeck measurement

3.3.1 Standard Operating Procedure (SOP)

The newly improvised apparatus that has been developed need to follow some procedure to be operated. This is crucial to make sure that the apparatus can be used for a long period. Therefore, a standard operating procedure (SOP) has been created for this chamber usage. The SOP implementation before and during the usage of this apparatus are as below:

1. Setting sample, probe and thermocouples properly.
2. Test water flow by opening the chiller valve.
3. Clear all the bubbles in the cooler.
4. Make sure there is no leakage.
5. Close the chamber door.
6. Turn on the pump machine. Make sure that the venting valve is closed before turning on the vacuum pump.
7. Pump the chamber for a while (5 – 10 minutes) to achieve the highest vacuum pressure (~ 20 mbar).
8. Turn on and set the heater controller.
9. Increase the temperature step by step (50^{o}C at times) to prevent an overshoot of the heater.
10. Start testing.

The SOP of the apparatus after completing the measurement of thermoelectric materials are shown below:

1. Once the chamber is vacuumed to maximum pressure, open all of the vacuum door stoppers.
2. Turn off the heater switch, and cool the chamber until reaches room temperature.
3. Turn off the vacuum pump.
4. Start venting, open the venting pump.
5. Once it achieved atmospheric pressure, the door will be opened.

3.4 Samples

Thermoelectric samples used in this study were doped with Bi_2Te_3- and PbTe-based materials. The sample was constructed into thermoelement samples from powder raw material. The measured powder was hot-pressed at different pressure, temperature and holding times. There were 8 samples (A-H) prepared for this study as shown in Table 3.2.

Table 3.2 shows that there are 2 n-type target composition samples which are n-$Bi_2Te_{2.7}Se_{0.3}$, n-$PbTe_{0.8}Se_{0.2}$ and 2 p-type target composition samples which are p-$Bi_{0.5}Te_{1.5}Se_3$ and p-$Pb_{0.4}Sn_{0.6}Te$. both types undergo hot press under a pressure of 13 MPa and 20MPa. For Bi_2Te_3-based samples, the temperature during hot press is set at 473 K due to its low melting point, meanwhile, PbTe-based samples are set to 493 K and 523 K for 13 MPa and 20 MPa respectively.

Table 3.2: Types of samples and hot press specification.

Samples	Target Compositions	Type	Place	Pressure (P), Temperature(T) and Holding Time(H)
A	$Bi_2Te_{2.7}Se_{0.3}$	n-type	USIM	P: 13 Mpa T: 473 K H: 17 min
B	$Bi_2Te_{2.7}Se_{0.3}$	n-type	UKM	P: 20 Mpa T: 473 K H: 30 min
C	$Bi_{0.5}Sb_{1.5}Te_3$	p-type	USIM	P: 13 Mpa T: 473 K H: 17 min
D	$Bi_{0.5}Sb_{1.5}Te_3$	p-type	UKM	P: 20 Mpa T: 473 K H: 30 min
E	$PbTe_{0.8}Se_{0.2}$	n-type	USIM	P: 13 Mpa T: 493 K H: 17 min
F	$PbTe_{0.8}Se_{0.2}$	n-type	UKM	P: 20 Mpa T: 523 K H: 30 min
G	$Pb_{0.4}Sn_{0.6}Te$	p-type	USIM	P: 13 Mpa T: 493 K H: 17 min
H	$Pb_{0.4}Sn_{0.6}Te$	p-type	UKM	P: 20 Mpa T: 523 K H: 30 min

3.4.1 Samples Fabrication using Atomic Mass (AM) Method

Thermoelements were constructed from raw powders in bulk. Initially, the required size of thermoelements samples was a cube with dimensions 0.4 x 0.4 cm with various thicknesses of 0.2 – 0.4 cm. The samples were developed by using a cylinder mould with a diameter and height of 2.5 cm and 5.0 cm respectively as shown in Figure 3.9. Meanwhile, Figure 3.10 shows the mould that is used in fabricating the samples.

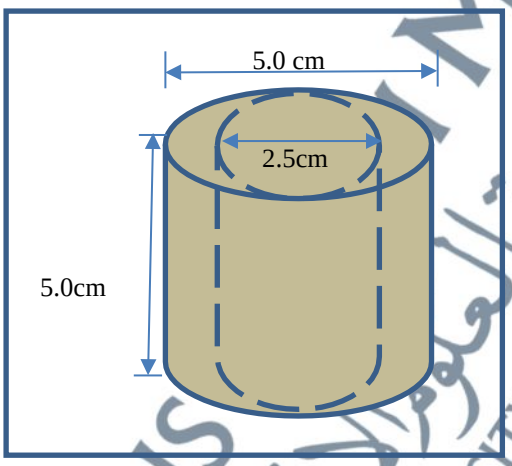

Figure 3.9: Mould size for the hot-pressing process

Figure 3.10: Mould used in fabricating samples

In this study, the fabricated samples were measured using 2 methods which are atomic mass (AM) and volume ratio (VR) methods. Figure 3.11 shows a flow chart of a process for each material calculated using the atomic mass (AM) method. To determine the mass of each raw material, the total molecular weight of the compound was determined based on the ratio of the composition of targeted stoichiometry. To estimate compound density, the percentage of each composition is calculated based on the molecular mass of the compound. From the estimated compound density, the mass of the compound is calculated with the given expected volume of sample. The mass of raw powder for each material can be determined using the calculated mass of the compound.

Since in calculation expected the volume of the samples, this can be calculated based on the size of the mould used. The mould used in this study is in a cylinder shape, therefore the required volume of sample required theoretically can be calculated using eq. 3.1.

$$V = \pi r^2 h \qquad (3.1)$$

For example, the required height of the n-type $PbTe_{0.8}Se_{0.2}$ sample is 0.4 cm, with the diameter of the mould being 2.5 cm so, the required volume would be 1.96 cm^3.

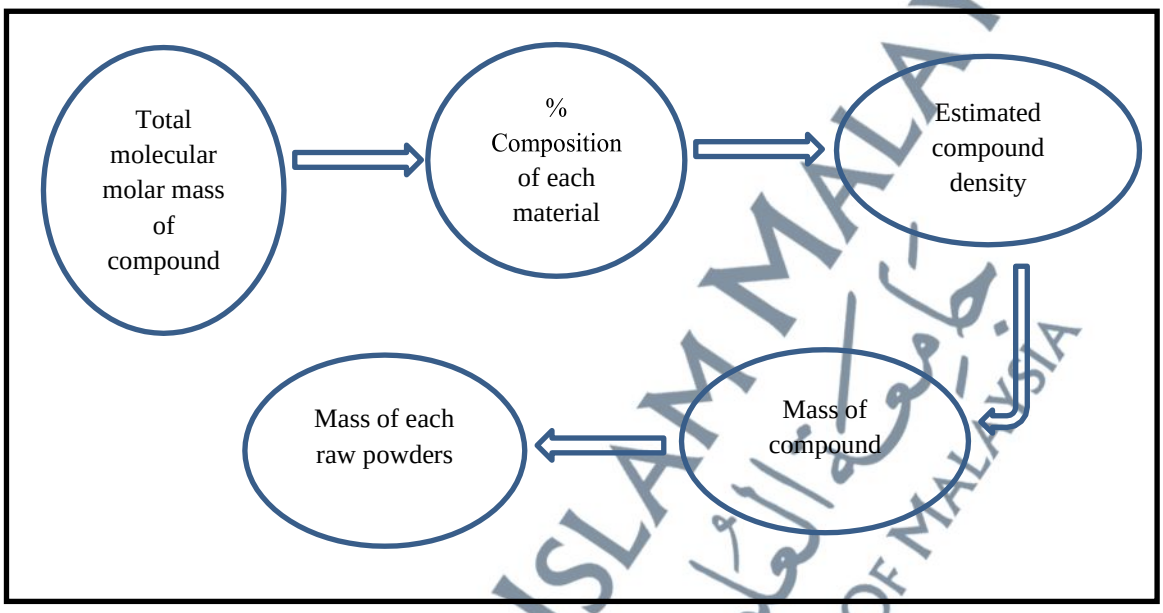

Figure 3.11: Flow for atomic mass (AM) method.

For further explanation, preparation of sample n-$PbTe_{0.8}Se_{0.2}$ using method AM was selected. Table 3.3 shows the calculation starts by calculating the total molecular molar mass of n-$PbTe_{0.8}Se_{0.2}$. To calculate this atomic mass of each material in the composition will be multiplied by its stoichiometry ratio.

Table 3.3: Calculation of molecular molar mass for $PbTe_{0.8}Se_{0.2}$ sample.

Materials	**Atomic Mass (g/mol)**	**Total Molecular Molar Mass (g/mol)**
Lead (Pb)	207.2	(1 x 207.2) + (0.8 x 127.6) + (0.2 x 78.96) = **325.07**
Telluride ($Te_{0.8}$)	127.6	
Selenide ($Se_{0.2}$)	78.96	

From the calculated total molecular molar mass, the percentage of composition for each material was determined. The calculation of percentage composition can be calculated from the atomic mass of each material composition divided by the total molecular molar mass of the compound as shown in Table 3.4.

Table 3.4: Calculation percentage composition of n- $PbTe_{0.8}Se_{0.2}$ sample.

Materials	**Atomic Mass Composition (g/mol)**	**% Composition = (atomic mass composition/ total molecular molar mass)**
Lead (Pb)	207.2 x 1 = 207.20	$\frac{207.20\ g/mol}{325.07\ g/mol} \times 100 = 64$
Telluride ($Te_{0.8}$)	127.6 x 0.8 = 102.08	$\frac{102.08\ g/mol}{325.07\ g/mol} \times 100 = 31$
Selenide ($Se_{0.2}$)	78.96 x 0.2 = 15.79	$\frac{15.79\ g/mol}{325.07\ g/mol} \times 100 = 5$

With knowledge of material density, the estimation of compound density can be determined by material density x %composition. Table 3.5 shows the calculation of the compound density.

Table 3.5: Estimated compound density of compound $PbTe_{0.8}Se_{0.2}$.

Materials	**Density (g/cm^3)**	**Estimated Compound Density (g/cm^3) = (material density x %composition)**
Lead (Pb)	11.34	(11.34 x 0.64) + (6.24 x 0.31) + (4.81 x 0.05) = **9.43**
Telluride ($Te_{0.8}$)	6.24	
Selenide ($Se_{0.2}$)	4.81	

Thus, the mass of the compound is calculated based on a formula $\rho = m/v$ where the volume needed is calculated using Eq. 3.1.

$$\boldsymbol{Mass\ of\ compound = Estimated\ Density\ of\ compound\ x\ (Volume\ needed)}$$

$$= \mathbf{9.43}\frac{\boldsymbol{g}}{\boldsymbol{cm^3}}(\mathbf{1.96}\ \boldsymbol{cm^3})$$

$$= \mathbf{18.48}\ \boldsymbol{g}$$

Therefore, the mass of each material can be determined by % of composition x mass of compound as shown in Table 3.6.

Table 3.6: Mass for each material for sample n- $PbTe_{0.8}Se_{0.2.}$

Materials	**% Composition**	**Mass of Material (g) = (% Composition x mass of compound)**
Lead (Pb)	64	0.64 x 18.48 = 11.83
Telluride ($Te_{0.8}$)	31	0.31 x 18.48 = 5.73
Selenide ($Se_{0.2}$)	5	0.05 x 18.48 = 0.92

To confirm this method, after the construction of the samples, the density obtained from a constructed sample is measured by comparing the properties of size and total mass with the required properties. Based on the newly constructed sample, another sample is constructed again with the density to reconfirm it. Therefore, this new density can be used to fabricate other structures or segmented samples. The measured mass and volume of the constructed sample are used to calculate the new density. For example, the measured mass and volume of the fabricated sample are 17.65 g and 2.11 cm^3 respectively. Therefore, the new density calculated was 8.36 g/cm^3. The new density of 8.36 g/cm^3 is close to the value of PbTe density which is 8.16 g/cm^3.

3.4.2 Sample Fabrication using Volume Ratio (VR) Method

The second method used to fabricate samples using HP is the VR method shown in Figure 3.12. Meanwhile, based on volume preoccupied with the material is shown below. The mass of materials needed to fabricate the samples is determined from the

density and size of the sample according to the formula: $\rho = m/v$; where density, ρ and volume, v of the sample. Since the samples are made from a different composition of materials. The calculation of amount of powder needed is shown by calculating the density of the mol compound before determining the mass of each material at the expected volume. The mass of the compound per 1 cm^3 is equal to the density of the mol compound.

For example, the density of n-$PbTe_{0.8}Se_{0.2}$ calculated from VR as shown in Table 3.7 which is equal to 8.65 g/cm^3. Calculated from the total mole of the compound is 2 with each material having a different ratio to form the compound. Therefore, to find the volume for each material, the 1 cm^3 volume will be divided by the total ratio of the compound.

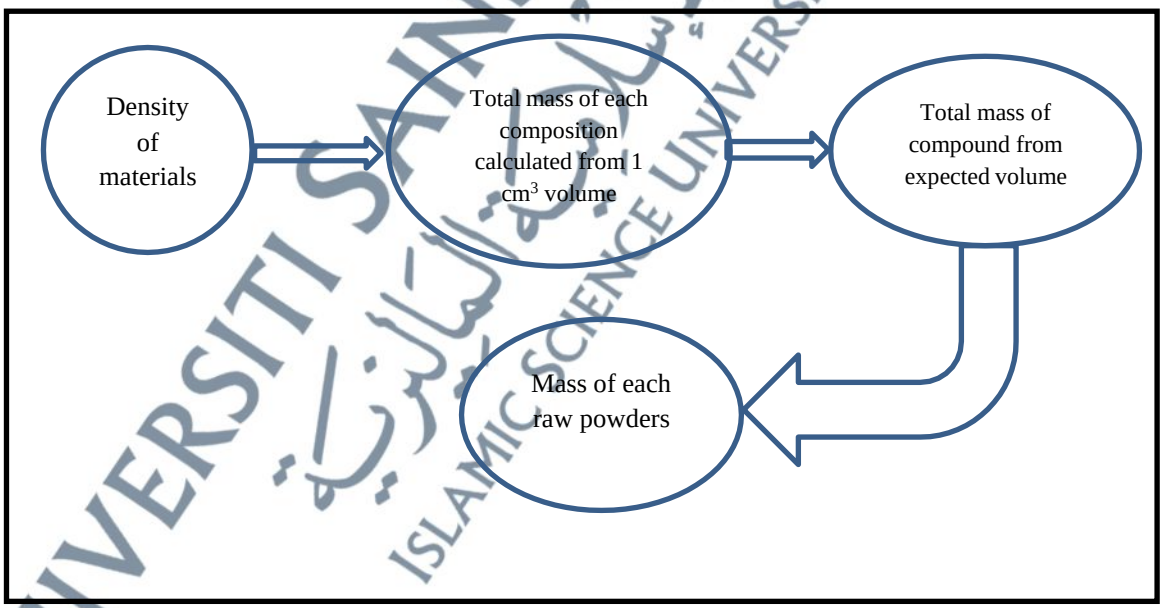

Figure 3.12: Flow chart for volume ratio (VR) method.

Table 3.7: Density of the compound $PbTe_{0.8}Se_{0.2}$

Materials	**Density (g/cm^3)**	**Volume per 1 cm^3** = $\left(\frac{1\ cm^3}{Total\ ratio\ of\ compound}\ x\ Ratio\ of\ each\ composition\right)$	**Mass per 1 cm^3 (g)** $(\rho = m/v)$
Lead (Pb)	11.34	$\frac{1\ cm^3}{2} \times 1 = 0.5$	$\frac{11.34\ g}{cm^3} \times 0.5\ cm^3 = 5.67$
Telluride ($Te_{0.8}$)	6.24	$\frac{1\ cm^3}{2} \times 0.8 = 0.4$	$\frac{6.24\ g}{cm^3} \times 0.4\ cm^3 = 2.50$
Selenide ($Se_{0.2}$)	4.819	$\frac{1\ cm^3}{2} \times 0.2 = 0.1$	$\frac{4.819\ g}{cm^3} \times 0.1\ cm^3 = 0.48$
			The total mass/1 cm^3 = **8.65**

The mass of each material for a given volume obtained using the given density that has been calculated. The required volume of the sample is 1.72 cm^3 as shown in eq. 3.1. Therefore, the mass of the compound of n-$PbTe_{0.8}Se_{0.2}$ required for the above sample size is calculated as:

$$Mass\ of\ compound, m = \frac{Total\ mass}{1\ cm^3}\ X\ Volume\ sample \quad (3.2)$$

$$= \frac{8.65\ g}{cm^3}\ X\ 1.72\ cm^3$$

$$= 14.88\ g$$

The calculated mass required to form the sample is shown in Table 3.8.

Table 3.8: Mass required for sample n-$PbTe_{0.8}Se_{0.2}$ using ratio method.

Materials	**Powder mass (g)**
Lead (Pb)	$\frac{14.88g}{2} \times 1 = 7.44$
Telluride ($Te_{0.8}$)	$\frac{\cancel{14.88\ g}}{2} \times 0.8 = 5.95$
Selenide ($Se_{0.2}$)	$\frac{\cancel{14.88\ g}}{2} \times 0.2 = 1.49$

After the raw powder was successfully measured using both methods, the powders were then mixed by hand stirring before the hot-pressing process take place in2 different places. There were 2 types of hot press used in this study which are at UKM(Figure 3.13) with the ability of pressure 20 MPa pressure and at USIM with 13 MPa pressure. The hydraulic hot press in UKM is a manually hydraulic hot press machine while the hot press from USIM (Figure 3.14) is the automatic machine in which the pressure was fixed.

The setting temperature of the hot press in USIM for both Bi_2Te_{3-} and PbTe-based samples were 473 K and 493 K respectively. The temperature used was below the melting point of the doped element which is 493 K and 504.9 K for selenium (Se) and tin (Sb) respectively. The holding time for both HP settings in USIM and UKM differed because of the mould used. Initially, the holding time for the pressing process would be the same in both USIM and UKM machines. However, the holding time of 17 minutes at USIM due to the mould becoming bent before reaching the 30 minutes of holding time.

The size and mass of hot-pressed bulk samples (Figure 3.15) were then measured and the density was calculated. The thickness of samples was measured using a digital vernier calliper shown in Figure 3.16. The error of physical characteristics between constructed samples with the required characteristics was calculated and shown in Chapter 4. In addition, the samples were then sent to Chemist Laboratory in USIM to test their composition using EDS.

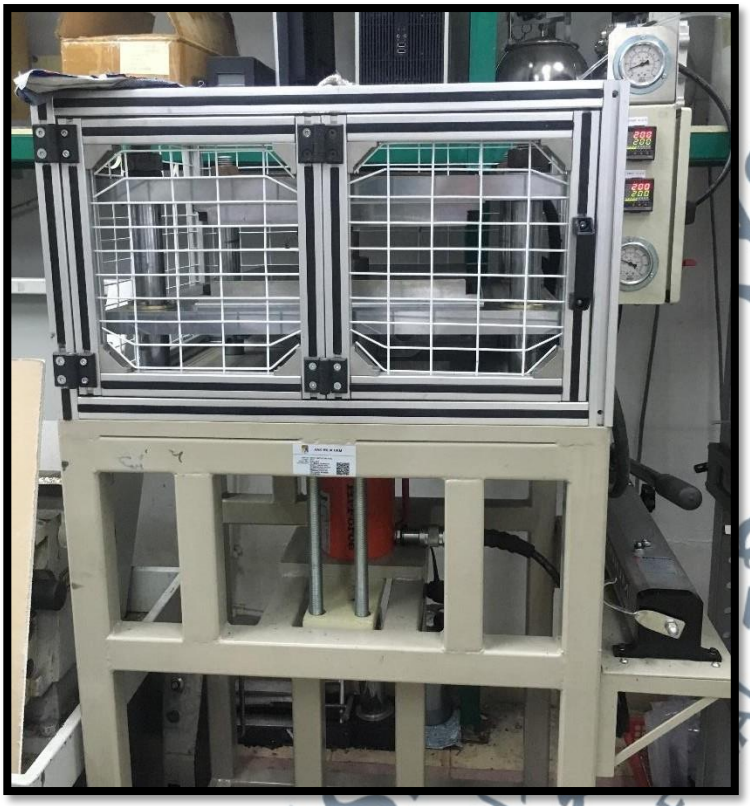

Figure 3.13: Hot Press machine in UKM.

Figure 3.14: Hot Press machine in USIM.

Figure 3.15: Hot pressed thermoelectric sample.

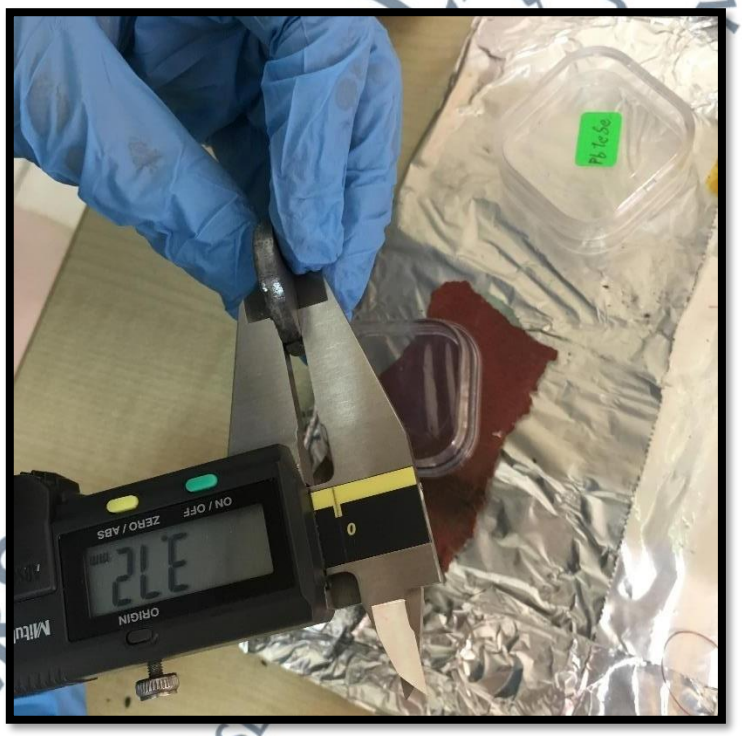

Figure 3.16: Measurement of the thickness of the sample.

3.5 Measurement

All successfully fabricated samples were then measured for their thermoelectric properties. The properties are electrical resistivity, Seebeck coefficient at the large and small temperature difference (ΔT) and last but not least its compositions. Table 3.9 shows the types of equipment used for these measurements.

Table 3.9: Types of equipment for thermoelectric measurement

Equipment	Purpose	Location
Hot Press USIM (Scientific LabTech) Hot Press UKM (Custom hydraulic press)	Fabrication	USIM and UKM
4-point Probe (Jandel RM3000+)	Electrical Resistivity	USIM
Hot Probe Setup (Home-made setup)	Seebeck Coefficient at low and high temperature	USIM
High-Temperature Vacuum Chamber (Improvise design)	Seebeck Coefficient at high temperature	USIM
EDS (Joel JSM-7800F)	Sample Compositions	USIM

3.5.1 Energy Dispersive Spectroscopy (EDS)

The material composition of samples is analysed using an EDS machine. Scanning Electron Microscope (SEM) is used in combination with EDS to capture an image of the sample's surface using an electron beam. This commercial equipment analysed the amount of elemental composition located at the surface. In addition, the identification of elements in the samples is obtained. This measurement was done by an expert to ensure that the results are in the best condition.

3.5.2 Seebeck Coefficient

Seebeck coefficient of the samples is measured using self-setup equipment. This self-setup equipment measured the Seebeck coefficient of samples under large and small temperature differences. The equipment consists of a copper block, cartridge heater, K-type thermocouples, power supply, thermoelectric module, multimeter and PicoLog data logger. The arrangement of the equipment is shown in Figure 3.17. To reduce heat loss to surrounding around the samples, the wool insulator is used to cover up the samples.

On the hot side of the copper block, the cartridge heater is connected to a transformer that can regulate the heater's voltage supply. For example, the voltage on the transformer is set to 25 V which results in the heater being 310 K after several minutes. Later, the voltage is increased to 100 V, and then the temperature of the heater is measured when it reaches stability in about 30 minutes to 1 hour in each increment. A k-type thermocouple is used to measure temperature for both sides of the copper block. The thermoelectric sample was situated in between the copper

block, and the cartridge heater was located on the top side of the copper block which determined the hot side of the block. As for the cold side, the thermoelectric module was used for the Seebeck measurement under a small temperature difference. The insulator cotton wool was used surrounding the samples to prevent heat loss to the surrounding. All measurements are recorded in Chapter 4.

Seebeck coefficient under large temperature difference is compared to the measurement using high-temperature vacuum chamber apparatus. This is to study the effect and difference of Seebeck value between both apparatuses.

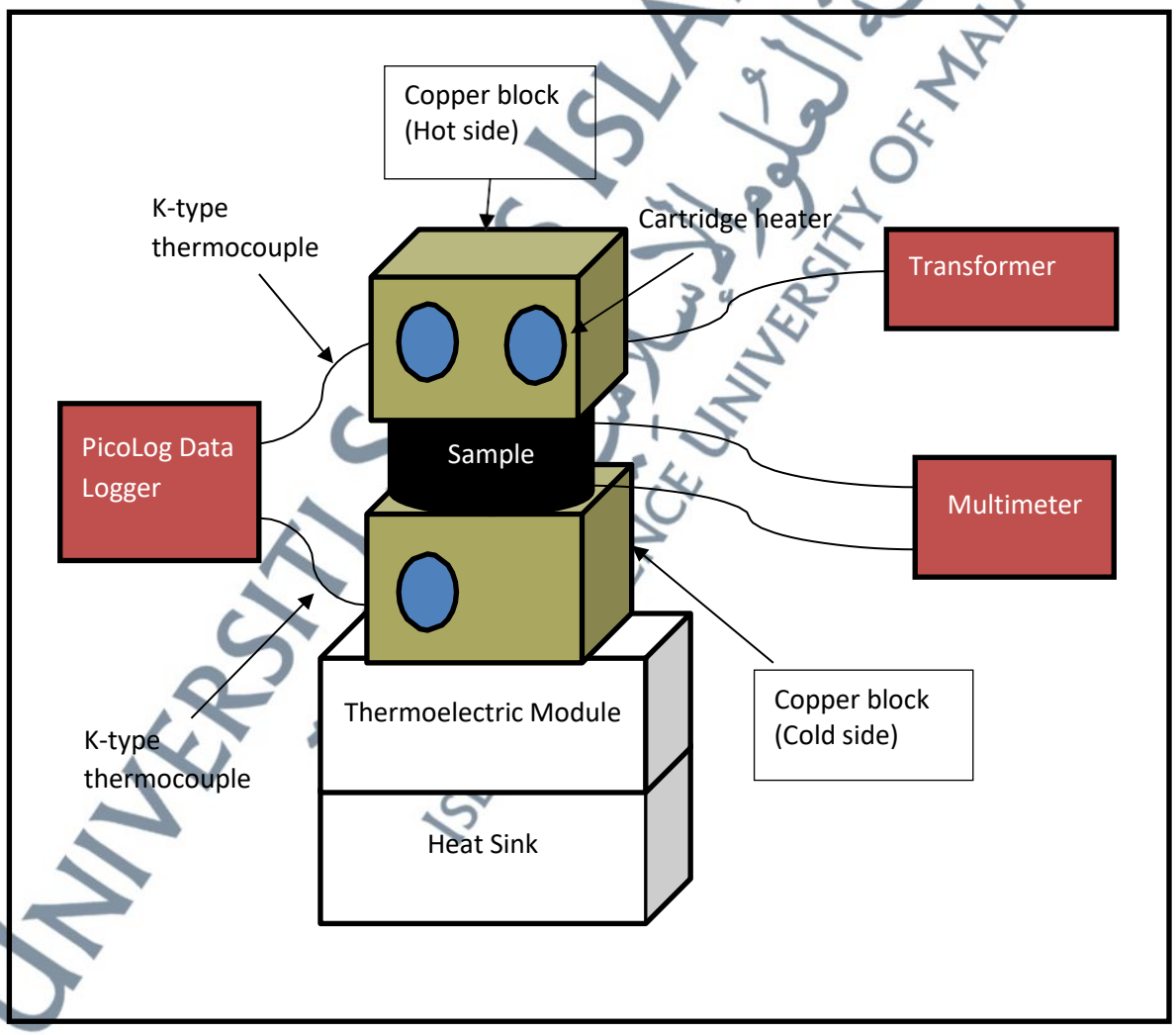

Figure 3.17: Self-setup apparatus for Seebeck coefficient

3.5.3 Electrical Resistivity

The electrical resistivity of samples was measured using a 4-point probe (Jandel RM 3000+) shown in Figure 3.18. This equipment is used to measure the electrical resistivity at the surface of a sample. The surface of the samples was polished using sandpaper before putting it under 4-point probe apparatus. The polish step is to remove the oxidation layer that occurred on the surface of samples. Before the electrical resistivity measurement can be done, a 4-point probe needle needs to touch the surface of the sample as shown in Figure 3.19 so that the current can be applied to the sample. Adjustment of the height of the probe needs to be done in every measurement for each sample due to the different thicknesses of the samples. The measurement was repeated 3 times for each sample to get the average measurement. The current supply of this equipment is limited to 100 mA.

During the sample placement, the equipment is set to standby mode so that there is no current flow. Subsequently, the current is supplied for 10 mA then sheet resistance, *Rs* of sample is measured which appeared as R/sq in a unit of Ω/sq. The bulk resistivity can then be is calculated using the equation 3.3 below:

$$Bulk\ Resistivity, R\ (\frac{\Omega}{cm}) = Height, H\ (cm) * \ Resistance, Rs\ (\frac{\Omega}{sq}) \quad (3.3)$$

Where *H* is the thickness of bulk in cm. The average of resistance is obtained before the resistivity is calculated.

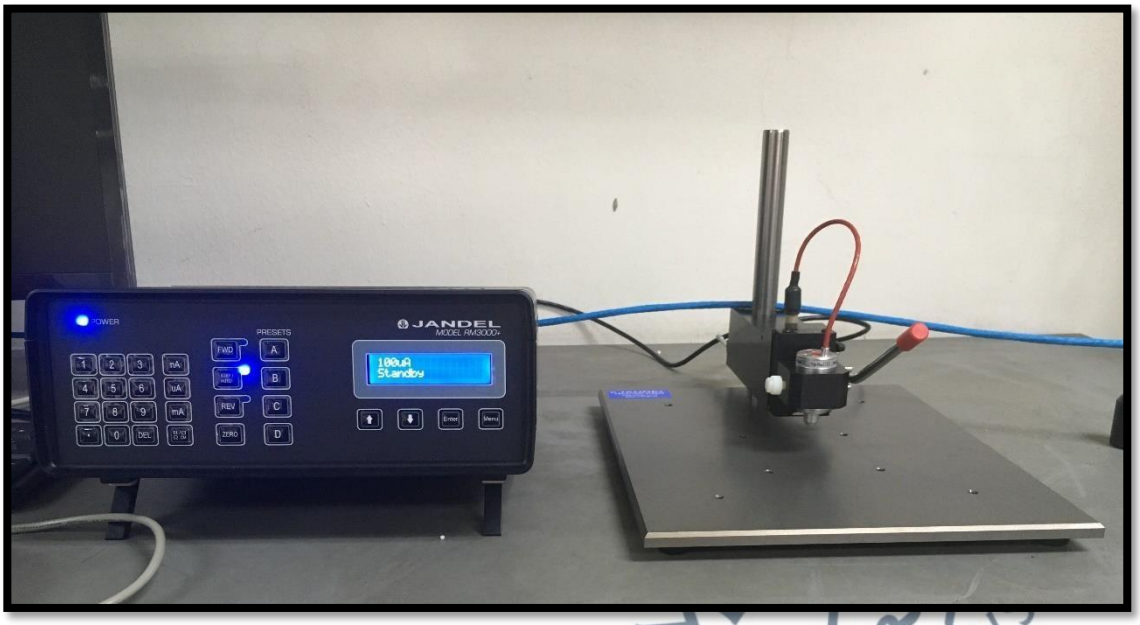

Figure 3.18: Jandell RM3000+ 4-point probe.

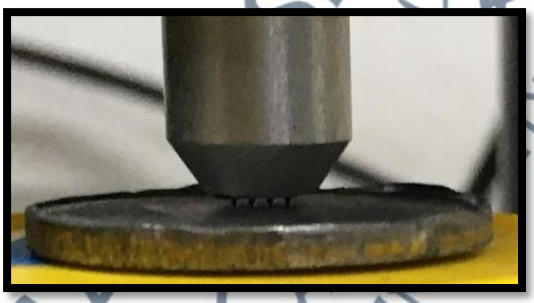

Figure 3.19: 4-point probe needle during the measurement.